# Observation of molecular emission bands in cw He-Cd$^+$ hollow-cathode lasers

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Molecular emission bands accompanying all atomic laser transitions have been observed in a cw He-Cd$^+$ hollow-cathode laser. They appear as an asymmetrical broadening around the atomic laser transitions, which can extend as far as 90 nm for the case of blue emission. Their dependence on discharge conditions has been studied in depth under lasing conditions, and the results show that they are strongly related to the laser processes. These molecular bands do not originate from $He_2$ and $Cd_2$ dimers, but can be associated with (He-Cd$^+$)* complexes. The observation of molecular emission bands, under lasing conditions, suggests the existence of population mechanisms different from those previously accepted.

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## I. INTRODUCTION

Hollow-cathode He-Cd$^+$ lasers have been studied for a long time since their first successful operation in 1965 [1]. The main interest in this kind of laser is its capability to deliver white light, which was achieved for the first time in 1975 by Fujji, Takahashi, and Asami [2]. Since then, several new configurations have been proposed in order to improve laser output characteristics [3–6] and a commercial He-Cd$^+$ white-light laser is now available [7]. While extensive work has been carried out for He-Cd$^+$ lasers [1–11], there are still some open questions about the population mechanisms of the upper laser levels. In particular, some molecular features have been observed recently [9–11] which are not explained by the population mechanisms widely accepted so far. We have found molecular contributions due to $He_2$ and $Cd_2$ dimers and some molecular features directly related to the laser action which are thought to be associated to the (He-Cd$^+$)* complex. Evidence of these molecular features, their dependence on discharge conditions, as well as their relation to laser processes, are given in this paper. We center our work around the green and blue laser transitions in which molecular features could be studied over a wide range of operating parameters.

The Cd$^+$($4f$) levels (see Fig. 1) emitting the 537.8- and 533.7-nm green laser lines are the lower levels for red lines; thus it has frequently been concluded that the predominant population mechanism for the green lines is a radiative cascading from the $6g$ and $5g$ levels. However, electron-collision excitation from the Cd$^+$ ground state also plays an important role in the population of $4f$ levels. The $7p$, $6d$, and $4f$ levels lie together in near energy coincidence and their populations are mixed by collisions with thermal electrons; thus the most likely Cd$^+$($4f$) excitation channel by electron collisions is [6]

$$\mathrm{Cd}^+ + e \rightleftharpoons \mathrm{Cd}^{+*}(7p) + e \ , \quad (1)$$

$$\mathrm{Cd}^{+*}(7p) + e \rightleftharpoons \mathrm{Cd}^{+*}(6d) + e \rightleftharpoons \mathrm{Cd}^{+*}(4f) + e \ . \quad (2)$$

Boulmer-Leborgne, Dubreuil, and Pellicer [6] have attributed 60% and 40% contributions to radiative cascade and electron collision, respectively, at the maximum of the line emission. However, these mechanisms do not fully explain the observed difference in the behavior of green and red lines as a function of pressure [4,5,9–11]. Thus a further population mechanism has been proposed [4], namely, resonant energy transfer from molecular

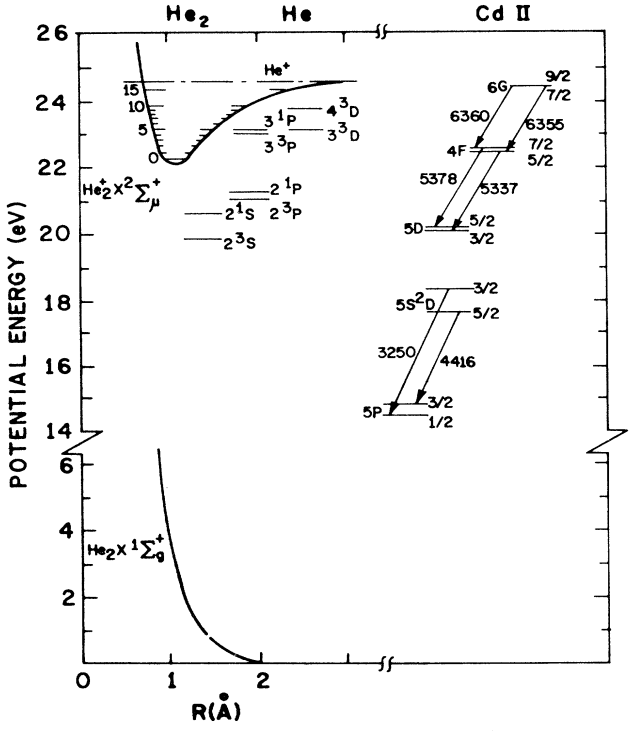


FIG. 1. Partial energy-level diagram for Cd$^+$, relevant for the He-Cd$^+$ laser. Some energy levels for He and $He_2$ are also indicated.

 

$He_2^+$ to the $4f$ levels in $Cd^+$ according to

$$He^+ + 2He \rightleftharpoons He_2^+ + He \ , \quad (3)$$

$$He_2^+ + Cd \rightleftharpoons Cd^{+*}(4f) + 2He \ . \quad (4)$$

We have found molecular emission bands around the green laser transitions which appear as an asymmetrical broadening around the atomic transitions; these bands cannot be explained by the above excitation mechanisms but can be associated with the generation of the $(He\text{-}Cd^+)^*$ complex.

For the case of blue transitions, it is now accepted that in a hollow-cathode discharge the upper states of the blue line (441.6 nm) are populated predominantly via Penning excitation and electron collision excitation according to [4,6]

$$He_m^* + Cd \rightleftharpoons He + Cd^{+*}(5s^2) + He + e$$

(Penning excitation) , (5)

$$e + Cd \rightleftharpoons Cd^{+*} + 2e \quad \text{(electronic excitation)} \ . \quad (6)$$

Boulmer-Leborgne, Dubreuil, and Pellicer [6] attribute 25% to Penning excitation and 75% to electronic excitation, while Grey Morgan, Hopkin, and Telle [4] found contributions of 60% and 40%, respectively. As for the green laser line, a strong molecular contribution is also observed around this line, under lasing conditions, which is not explained by these population mechanisms. Therefore a different excitation process should be proposed.

## II. EXPERIMENTAL SYSTEM

The laser-tube design used for these measurements is a multisegmented $He\text{-}Cd^+$ hollow cathode with a total discharge length of 60 cm. The schematic diagram of the experimental setup is shown in Fig. 2. The laser usually operates at gas pressures in the range 3–50 mbar and at a typical total discharge current of 1.3 A. The cavity consists of two concave high reflectors ($R \geq 99.5\%$). Details of the configuration are given elsewhere [5,9,10].

Spectroscopic measurements have been carried out under lasing conditions, in contrast to the majority of the reported work, in which only total laser powers are measured or spectroscopic studies are performed under nonlasing conditions.

Besides numerous lines of neutral He and Cd and ionic $He^+$ and $Cd^+$, strong molecular features are observed in the spectra. Figure 3 shows typical spectra in the region 420–820 nm under lasing and nonlasing conditions. One can see from this figure that molecular features are present for lasing conditions (they appear as an asymmetrical broadening around all laser transitions) but disappear under nonlasing conditions (misaligning one mirror while maintaining all discharge conditions unchanged). The fact that molecular features disappear under nonlasing conditions suggests a mechanism involving $(He\text{-}Cd^+)^*$ complexes rather than $He_2$ or $Cd_2$ dimers.

The main objective of this work was to find the role that these molecular emission bands play for the laser transitions. For this purpose, measurements of molecular contribution were carried out as a function of He pressure (3–50 mbar), discharge current (60–150 mA/anode), He flow rate (0.5–3.0 lt/min), and Cd vapor pressure (0.003–0.26 mbar). The study was undertaken for the blue and green lines. For these, the molecular contribution could be studied over a much wider range of the laser parameters than was possible for the red and ir transitions. This is due to the particular coatings of the laser mirrors used in this study.

Molecular emission bands, originating from the $He_2$ and $Cd_2$ dimers, have also been observed under nonlasing conditions. Their dependence on discharge conditions as

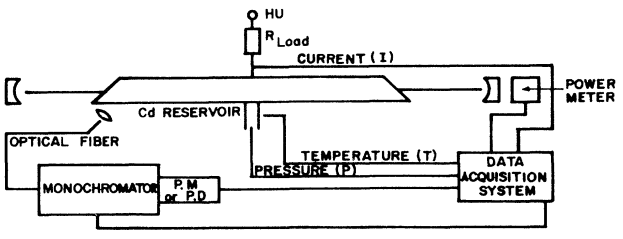


FIG. 2. Schematic diagram of the experimental setup.

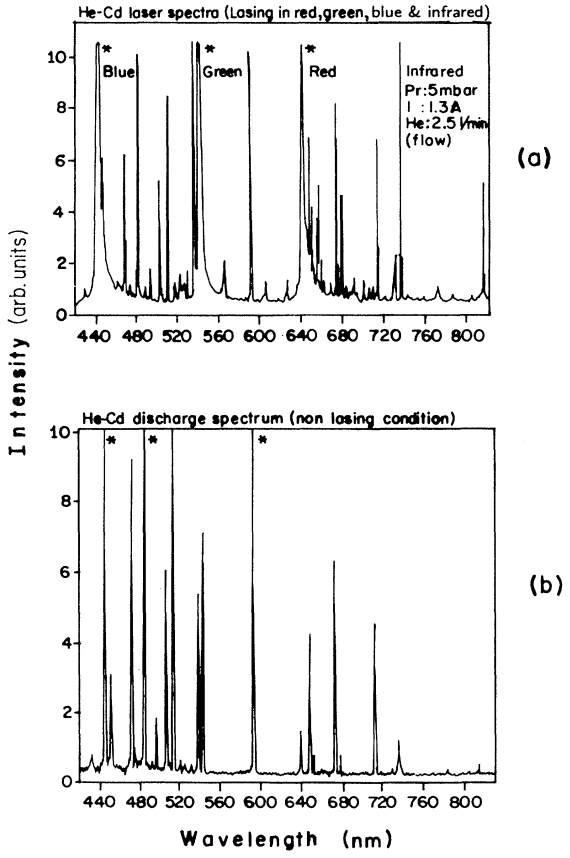


FIG. 3. Typical spectra obtained from the $He\text{-}Cd^+$ hollow-cathode laser in the 420–820-nm wavelength range under (a) lasing and (b) nonlasing conditions. Molecular emission bands around each laser transition are clearly seen under lasing conditions. The asterisks denote saturation of the spectral feature on the scale of the figure.

well as their relation to laser emission are discussed below.

## III. $He_2$ BANDS

Molecular emission bands originating from the excited $He_2$ dimer have been observed. These bands are thought to be largely generated during recombination from $He_2^+$. The pressure dependence of the related fluorescence is in line with the role molecular $He_2^+$ ions play in the generation of the green He-$Cd^+$ laser transitions [12].

The formation process for $He_2^+$ molecular helium ions is via several mechanisms:

(a) Direct formation of molecular $He_2^+$ ions from a pair of helium metastables as follows [13]:

$$He^* + He^* \Longrightarrow He_2^+ + e \ . \tag{7}$$

(b) Collision of a metastable atom with two ground-state helium atoms according to

$$He^* + 2He \Longrightarrow He_2^* + He \ , \tag{8}$$

$$He_2^* + (e + E_{kin} \sim 15 \text{ eV}) \Longrightarrow He_2^+ + 2e \ . \tag{9}$$

(c) Three-body collisions [14]:

$$He^+ + 2He \Longrightarrow He_2^+ + He \ . \tag{10}$$

The generation of $He_2$ molecular emission bands can be written as

$$He_2^+ + e + A \Longrightarrow He_2^{**} + A + \Delta E \ , \tag{11}$$

$$He_2^{**} \Longrightarrow He_2^* + h\nu_{band} \ , \tag{12}$$

where $He_2^{**}$ indicates a high-lying electronic state and $A$ may be any collision partner available in the discharge. It has been established [15] that generation of excited $He_2^{**}$ is most likely when $A$ is an additional electron.

$He_2$ bands around 620 nm are clearly seen in Fig. 4, where the helium pressure has been varied while maintaining all other discharge conditions unchanged. The spectra were recorded for a discharge in helium (the cadmium reservoir was not heated) and under the same conditions used for the helium-cadmium mixture in laser operation (He flow rate $=1$ l/min, discharge current $=1.3$ A).

Figure 5 shows the pressure dependence of the emission intensity for representative lines of the neutral and ionic atom species, as well as for molecular emission bands. Clearly, the intensity of $He_2$ molecular bands increases with pressure in contrast to the behavior of He and $He^+$.

## IV. $Cd_2$ DIMERS

The characteristic emission from the $Cd_2$ dimer centered around 470 nm has been observed. It is in agreement with the fluorescence band shape reported by Drullinger and Stock [16]. Figure 6 shows a comparison between the spectra of pure helium and helium-plus-cadmium discharges, in which the $Cd_2$ contribution is

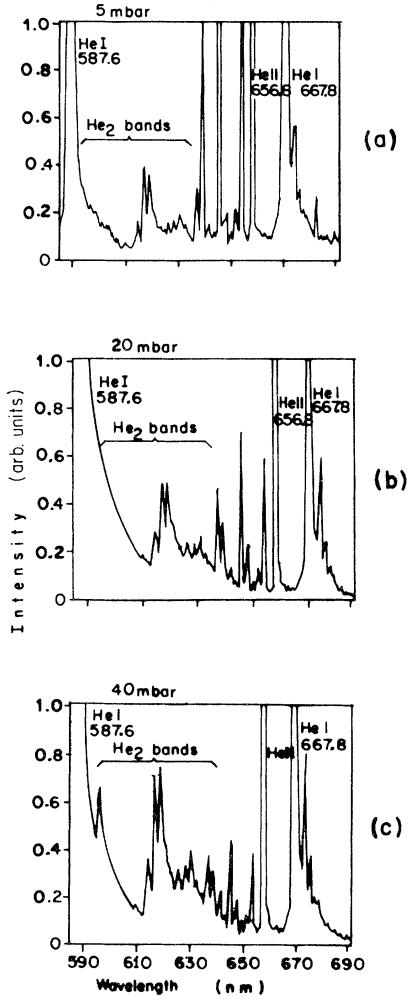


FIG. 4. $He_2$ molecular emission bands around 620 nm for a helium pressure of (a) 5, (b) 20, and (c) 40 mbar.

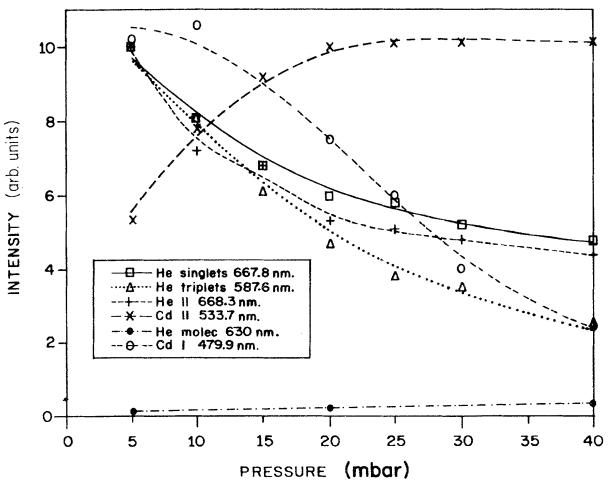


FIG. 5. Helium-pressure dependence of the emission intensity for $He_2$, $He^+$, He, $Cd^+$, and Cd.

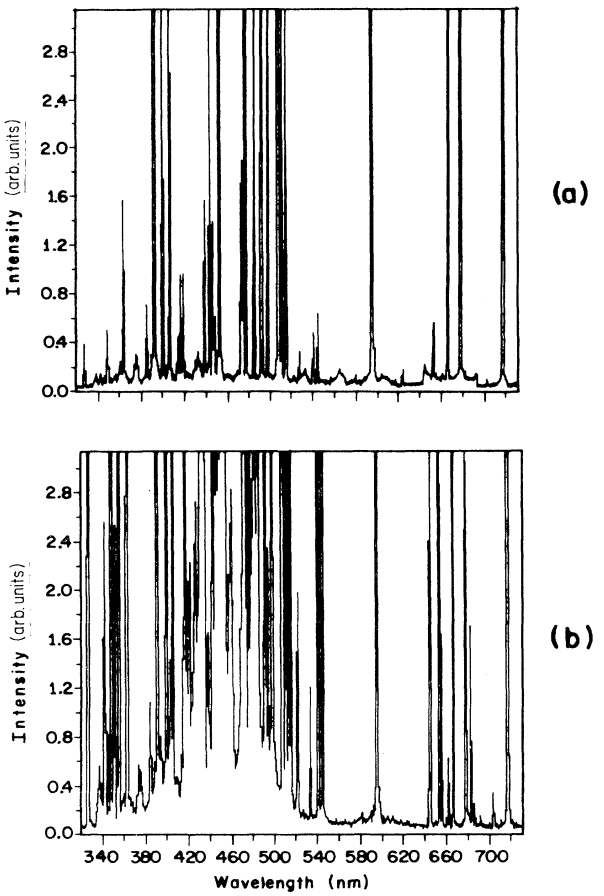


FIG. 6. Comparison between (a) a pure helium discharge and (b) a He-$Cd^+$ discharge, in order to show the $Cd_2$ molecular band appearing around 470 nm. Some lines are saturated on the scale of the figure.

clearly seen (it appears as a broad feature which extends from below 340 nm to beyond 520 nm, with maximum intensity around 470 nm). While the $Cd_2$ dimer can be observed under nonlasing conditions, it does not seem to play a recognizable role in the lasing process.

## V. (He-$Cd^+$)* MOLECULAR BANDS

Besides molecular features arising from $He_2$ and $Cd_2$ dimers, we have found a very strong molecular contribution directly related to the lasing process accompanying all atomic transitions but especially around the blue and green laser transitions. These molecular bands appear as an asymmetrical broadening on both sides of each atomic transition and under certain discharge conditions they can be the dominant process.

Figure 7 shows a sequence of spectra obtained from the He-$Cd^+$ hollow-cathode laser, lasing in (a) blue and (b) green. The spectra were taken for several helium pressures at a total discharge current of 1.3 A, helium flow rate of 1 l/min, and cadmium vapor pressure of 0.17 mbar. The pressure dependence of the molecular bands is clearly seen from the figure in which the third spectra represent the strongest molecular contribution. This corresponds to a He pressure of 15 mbar for the case of the blue transition and to 35 mbar for the green one. The molecular bands extend over more than 80 nm for the spectra in Fig. 7(a).

It must be emphasized that all spectra shown in Fig. 7 were obtained under lasing conditions, which is evidence of the strong relation between these molecular bands and the lasing process. In fact, as can be seen from Fig. 3, the molecular bands "disappear" under nonlasing conditions. The ratio between the atomic and the molecular emission remains roughly the same. This provides strong evidence that the excitation mechanism is most probably associated with the (He-$Cd^+$)* complex rather than with $He_2$ or $Cd_2$ dimers.

In a hollow-cathode discharge, the formation of a (He-$Cd^+$)* molecular complex, similar to an excimer, is very likely. These molecular complexes are formed by collisions between He and $Cd^+$ in large numbers. Metal vapor excimers have been reported by Pichler, Veza, and

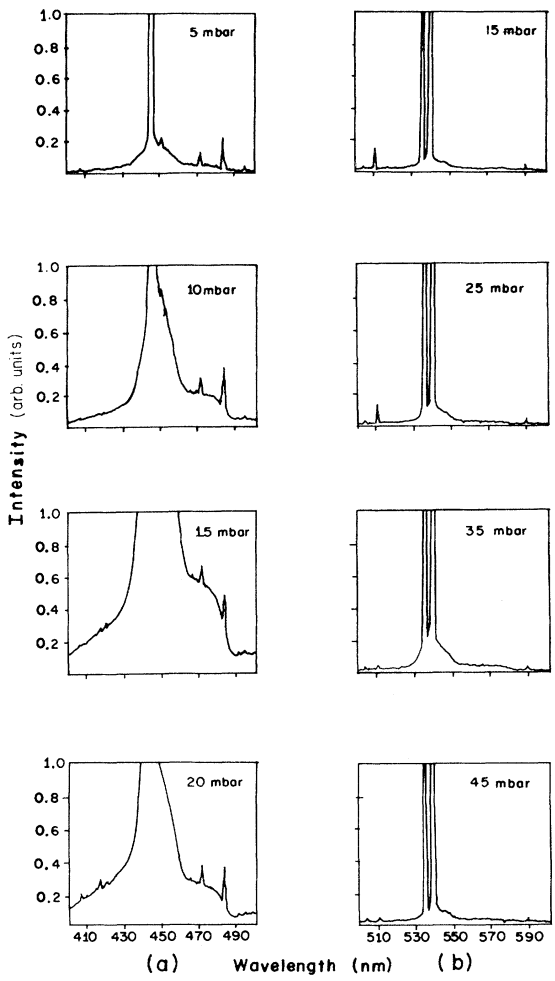


FIG. 7. Spectra obtained with a He-$Cd^+$ hollow-cathode laser showing the helium-pressure dependence of (He-$Cd^+$)* molecular emission bands around the (a) blue and (b) green laser transitions. The line center is saturated on the scale of the figure.

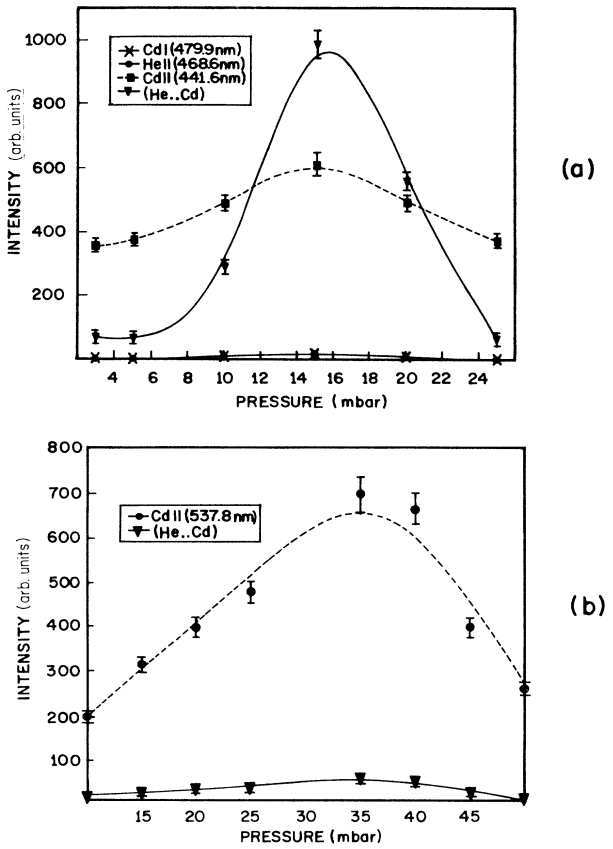


FIG. 8. Relative intensity of the (He-$Cd^+$)* molecular emission bands as a function of helium pressure, along with that due to atomic transitions, around the (a) blue and (b) green laser lines.

Fijan [17] formed in a high-pressure sodium lamp filled with a mixture of sodium, cadmium, and xenon. Hardly any information is available for other rare-gas–metal-ion complexes. One of the few examples is the broad emission band due to the (Ar-$Al^+$)* excimer near 193 nm that was recently observed [18]. However, neither theoretical nor experimental data are found in the literature for (He-$Cd^+$)*. Work is under way in order to determine the possible origins of the (He-$Cd^+$)* emission.

The helium-pressure dependence of the intensity of (He-$Cd^+$)* molecular emission bands is shown in Fig. 8. The intensity of the related atomic laser transitions is also shown, in order to compare the behavior of molecular and atomic emissions. It can be seen that the pressure dependence of molecular emission bands follows that of the atomic laser transitions, which proves that a relation exists among molecular bands and the lasing process. The contribution of (He-$Cd^+$)* molecular bands has been calculated by integrating the spectrum over the wavelengths at which they appear. The atomic contributions have been determined by integrating its line profile alone; this was achieved by convoluting the (unsaturated) line maximum with the spectral resolution function of the detection system.

TABLE I. Optimum discharge conditions for (He-$Cd^+$)* molecular emission bands.

| | Blue transition | Green transition |
|---|---|---|
| Discharge current (A) | 1.1 | 1.5 |
| Helium flow rates (l/min) | 1 | 1 |
| Cd vapor pressure (mbar) | 0.072 | 0.17 |

Spectroscopic measurements of (He-$Cd^+$)* molecular emission bands as a function of discharge current, helium flow rate, and cadmium vapor pressure have also been realized. The results are summarized in Table I, in which the optimum values for the (He-$Cd^+$)* complex formation and light emission are shown for the blue and green transitions.

## VI. CONCLUSION

An in-depth spectroscopic investigation to trace the role that molecular compounds of He and Cd play on the laser transitions of a He-$Cd^+$ hollow-cathode laser has been reported. Strong bands of $He_2$ were observed which were thought to be largely generated in the recombination from $He_2^+$. The resonant energy transfer from molecular $He_2^+$ to $4f$ levels in $Cd^+$ has been found to be an important mechanism in the generation of the green laser transitions. Light emission from $Cd_2$ dimers centered around 470 nm was found; however, $Cd_2$ does not seem to play a recognizable role in the lasing process. Finally, strong emission attributed to the (He-$Cd^+$)* complex has been observed, which is directly related to the lasing process. Molecular emission bands appear as an asymmetrical broadening around all laser transitions. Their dependence on discharge conditions has been studied in detail for the blue and green transitions.

All spectroscopic measurements have been carried out under lasing conditions; this is in contrast to the majority of the work reported by other groups. To our knowledge, a relation between (He-$Cd^+$)* molecular complexes and the lasing processes has not previously been recognized. This emphasizes the need to conduct spectroscopic studies of lasers under real operating conditions if we wish to deduce reliable information on the lasing processes from spectral data.

## ACKNOWLEDGMENTS

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